

On Micromechanisms of Hydrogen Plastification and Embrittlement of Some Technological Materials

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Abstract: Some fundamental problems of revealing micromechanisms of hydrogen plastification, superplasticity, embrittlement, cracking, blistering and delayed fracture of some technologically important industrial metallic materials are formulated. The ways are considered of these problems' solution and optimizing the technological processes and materials, particularly in the hydrogen and gas-petroleum industries, some aircraft, aerospace and automobile systems.

Key words: Hydrogen Plastification and Superplasticity, Hydrogen Embrittlement and Cracking, Industrial Metallic Materials, Micromechanisms, the Lewis Effect

INTRODUCTION

As has been formulated in Report [1] of the Basic Energy Sciences Workshop of the U.S. Department of Energy on Hydrogen Production, Storage and Use, in chapter Safety in Hydrogen Economy, corrosion and hydrogen embrittlement of materials are closely connected to details of their microstructure, and, in particular, to the segregation and diffusion processes that occur at internal interfaces and associated defects, such as dislocations; micromechanisms of such processes are not well understood. As has been also noted [1] in Potential Impacts, fundamental knowledge of hydrogen embrittlement of metals and welded joints would enable the setting of standards for the materials used in building a hydrogen infrastructure. As has been noted [1] in chapter Basic Research Challenges for Hydrogen Storage, fundamental research will be needed to understand materials' hydrogen degradation and failure processes to allow design of improved materials for hydrogen storage. Hence, Research Directions have been formulated by the U.S. DoE as: Understanding of the Basic Physics of Hydrogen Transport in Metals and Hydrogen-assisted Damage Mechanisms.

Fundamental Problems (A,B): (IA) One of the problems in question is revealing physics (micromechanisms) of the so-called "mechanical instability", i.e., a sharp plastification (up to superplasticity-like behavior and amorphization) of Fe, Pd, V, Ta, Nb, Zr, TiNi, Laves phases, Zr₃Rh in hydrogen atmosphere or under electrolytic hydrogen charging (the known experimental data (1982-2002), [2]).

(IIA,B) The second problem (related with IA) is revealing micromechanisms of the high pressure hydrogen influence on plasticity, strength, cyclic

fatigue, friction and wear of steels and other industrial alloys used in hydrogen power (the known experimental and technological data (1985-2003), [3]). (IIIA) The third problem (also related with IA) is revealing physics (micromechanisms) of the hydrogen plastification and hydrogen superplasticity of titanium and titanium-based industrial alloys (the known experimental and technological data (1985-2003), [4]). (IVB) On the other hand, the urgent problems are of physics (micromechanisms) of different hydrogen degradation, embrittlement, cracking and blistering of metals and industrial alloys (the experimental and technological data (1970-2003), [3-5]).

Solution Ways of Problems (A): The most data of Problems IA, IIA, IIIA can be interpreted on the basis of the use of challenging results [6-10], including a model of a periodic melting-like transition at grain boundary nanoregions (GBNR) under their "bombarding" by moving dislocations with hydrogen segregation "nanoatmospheres" and by deformation vacancies and complexes of vacancies with hydrogen atoms [11-21]. It is related to a periodic vacancy-hydrogen clustering (Y. Fukai *et al.* (1995-2001), [6]) at GBNR (a Frenkel type vacancy melting).

Solution Ways of Problems (B): The most data of Problems IIB, IVB can be interpreted on the basis of the use of challenging results [11-27]; some of them are the following.

Firstly [15, 20]: On the basis of analysis of the experimental data on apparent solubility and diffusivity of hydrogen in electrolytically charged maraging steel and iron-Armco, the hydrogen fugacity (pressure) of molecular hydrogen in metallic materials (under hydrogen charging) has been evaluated as $\sim 10^2$ - 10^3 bar,

for typical current densities of 10-100 A/m². The hydrogen fugacity of the same order of magnitude has been also estimated by using the deformation-mechanism maps with respect to the experimental data on blistering and cracking of low alloyed steel (under electrolytic hydrogen charging). It is consistent with the recent results on high pressure hydrogen generation by PEM electrolysis [28] and electrolytic production of ultra-high pressure hydrogen fuel without a compressor [29]. It can be used for experimental studies (modeling) of hydrogen permeability and hydrogen-assisted damage processes, which occur in compressed gas storage devices.

Secondly [11]: On the basis of the thermodynamic analysis and re-treatment of the most representative experimental data on solubility, electrical resistance and diffusivity of hydrogen in palladium specimens with high and low dislocation densities (including the Kirchheim and Flanagan distinguished data), it has been shown that the structure, composition, diameter (up to several nm), contribution to electrical resistance, thermodynamic and diffusion characteristics of the hydride-like segregation at dislocations in palladium can vary in a wide diapason depending on concentration and thermodynamic activity of hydrogen dissolved in the normal lattice of the metal. The formation of the hydride-like segregation at dislocations has place at large degrees of the undersaturation of the solid solutions with respect to the hydride precipitation in the normal lattice of palladium. It means that a specific phase diagram [27] can be considered for the system of "hydrogen – the near-dislocation segregation Pd-nanoregions", in comparison with the conventional phase diagram of "hydrogen – palladium".

The obtained results [11] can be used for a description of the apparent concentration and distribution of hydrogen between the normal crystalline lattice and the lattice defects' regions in palladium specimens produced by different ways of processing and treatment [19], for interpretation of the hydrogen influence on physical and mechanical properties of the materials [16,19] and also for revealing of the micromechanisms and ways of the optimization of regimes of the thermal-hydrogen treatment and governing hydro-phase hardening of palladium and palladium-based alloys [5,19]. Particularly, by using results [11-21], one can reveal in detail and quantitatively describe the Lewis effect micromechanism [30-33] (Appendix).

Thirdly [13, 21]: The known discrepancies in the apparent solubility and diffusivity of hydrogen in Fe and a maraging steel are mainly due to the formation at dislocations and grain boundaries of a complex hydride-like nanosegregation of Fe₂(C,N)H_{0.6-2} or Ni₃TiH_{1±δ} composition. It is related with the brittle intergranular failure and the stable cracking during the delayed steel fracture, which can be caused by a

periodical local phase transition (of a diffusion-martensite character) to the hydride-like structure [13, 16, 21].

Fourthly [22]: The Wagner theory of the internal oxidation (nitridation) of metallic alloys and the Lifshitz-Slyozov theory of the precipitate coarsening have been reconsidered (modified), in order to tentatively include the following aspects, particularly, for the case of the semi-coherent precipitates: (1)- the formation of high dislocation densities at the precipitate vicinity; (2)- the specific internal oxidation of the near-dislocation regions, several nm in diameter, by the impurity co-segregation; (3)- the influence of such "oxidized" dislocations on the apparent solubility and diffusivity of oxygen (nitrogen) and the solute metallic impurities in the host metal; (4)- the elastic stress contribution in the thermodynamic driving force which can stop the precipitate coarsening and even reverse it and lead to a shrinking of the precipitates; (5)- the dependence of the precipitate density and size over the depth of the oxidized zone; (6)- the influence of the dislocations and elastic stresses on the diffusion of the "excess" solvent atoms from the oxidation front toward the free surface; (7)- the creep rate of the oxidized zones. Typical experimental data on internal oxidation of Cu - 0.3 at. %Fe alloy and on internal nitridation of Ni - 5 at. %Cr alloy have been analysed. A large enhancement (by eight orders of magnitude) of the apparent product of the impurity (Fe or Cr) solubility and diffusivity in the matrix (Cu or Ni) has been shown at variance with the predictions of the classical (non-modified) theory.

Fifthly [23-27]: A critical analysis and interpretation has been done of numerous experimental data on diffusion anomalies of transition element solute diffusors (Fe, Mn, Cr, Ti, V, Zr, Sc, ...) in Al [14, 23, 24], the data on anomalous diffusion of carbon and nitrogen in cold-rolled Fe and steels [14, 23]. The interpretation of the anomalies is based on taking into account an available complex of data, both experimental and theoretical, concerning the non-conventional near-dislocation nanosegregates of the compound-like cluster structure (as Fe_{1.3}Al₃, Fe_{1.5}Al₆, Fe₂(C,N), where \square is the structural vacancy symbol), which can be characterized [14, 24-27] as linear adsorbed nanophases (LANP). It includes the consideration of the problem on impurity diffusion accompanying with a specific phase transition in the near-dislocation segregation nanoregions. The role of such segregation and elastic stresses has been considered for diffusion-assisted processes of the internal oxidation [22], nitridation [22], precipitate coarsening [22] and recrystallization [25] in metals. A special attention has been given to an open question on specific phase diagrams for LANPs, i.e. for segregation nanoregions of high pressures at dislocations in dilute

solutions of iron in aluminum and hydrogen in palladium [11, 24-27].

CONCLUSION

The results of such thermodynamic studies can be used for optimizing processes of the hydrogen embrittlement, cracking and delayed fracture of the materials.

It is related to the safety and standardization problems of metallic materials in the hydrogen and gas-petroleum industries, and also, - in some aircraft, aerospace and automobile systems.

It's relevant to emphasize the importance of such a non-conventional analysis of the related experimental, theoretical and technological data for revealing the micromechanisms and optimizing the technological processes and/or materials.

On the basis of results [6-27] a proposal can be submitted to the corresponding Grant Programs as: "Physics of hydrogen transport in metals and alloys and hydrogen-assisted damage micromechanisms".

Appendix: On the Lewis Effect Micromechanism:

As is described in [32], the macroscopic manifestation of Lewis effect [30, 31] occurs in the case of using a hydrogen charged palladium (palladium alloy) tube at the equilibrium state with gaseous hydrogen inside the tube. One end of the tube is closed, its other end is connected to a manometer fixing hydrogen pressure inside the tube. On the outside, the tube is subjected to an additional hydrogen charging either electrochemically (electrolytically) or from a gaseous phase (by a sharp increase in the outside hydrogen pressure). It results in a decreasing of the inside tube hydrogen pressure during an initial rather long stage of the charging, - therein lies a macroscopic outer manifestation of Lewis effect. As time passes, the hydrogen pressure inside the tube starts rising, i.e., there is set a normal process of hydrogen diffusive penetration through the tube wall.

As is also described in [32], the Lewis effect mechanism [30, 31] is related to the following schedule. At the first instants of a 'hydrogen shock', a metal outer surface layers expand sharply, and gradients of hydrogen concentration stresses and elastic deformations appear across the whole wall. As a result, there appears a thermodynamic driving force for the development of hydrogen uphill diffusion out of the inner volumes of the tube wall to its outer side being saturated with hydrogen. Hydrogen concentration in subsurface layers of the tube inner surface correspondingly decreases for the time being. An equilibrium with gaseous hydrogen inside the tube is disturbed. Hydrogen is being absorbed by a metal, and its pressure inside the tube decreases for a while [31, 32].

On the basis of the approaches and results [11-21], one can suppose a formation of a layer of a high density of fresh dislocations (that is dislocations non-decorated by the hydride-like nanosegregation) ahead of the moving hydrogen penetration front (when the outside additional charging of the tube [30, 31]). In this connection, a lot of known experimental data can be referred on a formation of a high dislocation density in metals and alloys under the electrolytic hydrogen charging [13, 15, 20]. According to [11-21], such a layer is characterized by both low hydrogen (apparent) diffusivity, and high hydrogen (apparent) capacity, in comparison with the material with low dislocation density (as it can be at the inner side of the tube). The formation of the hydride-like equilibrium nanosegregation at dislocations occurs in very dilute solutions of hydrogen in the palladium lattice, and the nanosegregation composition, size and structure depends on the hydrogen concentration in the palladium lattice [11]. Therefore, the moving front layer of high density of fresh dislocations can be charged (for a while) by means of hydrogen normal (not uphill) diffusion supply mainly from the inner side of the wall [30, 31], depending on the layer total thickness and the distance from the layer to the inner side of the tube. In this case, the composition, size and structure of the hydride-like nanosegregation at the dislocations corresponds (for a while) to the thermodynamic equilibrium with the very dilute solution of hydrogen in palladium lattice [11]. A long enough exposition results in the nanosegregation at the dislocations corresponding to the equilibrium with the external hydrogen pressure [11]. Such an interpretation is consistent with the experimental data [33]. By using such a model and the results [11-21], one can perform a quantitative description of the data [30, 31, 33].

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